Chemical Properties of the Heaviest Elements

Heavy Element Nuclear and Radiochemistry Group (HE)[1]

Lawrence Berkeley National Laboratory (LBNL)

Nuclear Science Division

The most fundamental goal in chemistry is the determination of the chemical properties of the elements. Information on the chemical properties of the heaviest elements can be used to assess the importance of relativistic effects in the valence electrons, and to refine theoretical calculations and our understanding of their chemical properties. Knowledge gained for the heaviest elements can be applied to understanding of chemical properties throughout the periodic table.

Isotopes of lawrencium (Lr, element 103) and heavier elements have half-lives of a few minutes or less, and can only be produced at accelerators. Production rates are low, ranging from one atom per minute to one atom per day. Because of these limitations, chemistry must be performed on single atoms, using extremely sensitive and specialized techniques. Therefore, relatively little is known about the chemistry of the heaviest elements. So far, there have been only five chemical experiments with seaborgium (Sg, element 106), one with bohrium (Bh, element 107), and one with hassium (Hs, element 108). For these three elements, only very general chemical properties have been measured, tentatively placing them in their groups 6, 7, and 8 of the periodic table, respectively. There have been a few dozen publications on experimental determination of the chemical properties of dubnium (Db, element 105) and rutherfordium (Rf, element 104). These more detailed results give tantalizing clues about the finer points of chemical bonding and stability of simple complexes, but are at times, contradictory.

Most of the heavy element chemical properties that have been measured to date resulted from experiments conducted by the LBNL team or where LBNL scientists played a substantial role in international collaborations (Germany, Switzerland, Russia, and Japan). These experiments represent the bulk of knowledge of chemical properties for six elements, from lawrencium (103) to hassium (108), and extended the periodic table by six percent. A brief summary of heavy element chemical knowledge is given in the appendix.

When producing isotopes of elements 103-108 at accelerators, large amounts of interfering radioactivities are produced concurrently. Until now, the most important aspect of a heavy element chemical separation was the need for an extremely efficient separation of the heavy element atoms from those interfering radioactivities. This severely limited the chemical reactions that could be used. We have pioneered the use of the Berkeley Gas-filled Separator (BGS) as a preseparator to provide high-purity heavy element samples for chemical separations. This allows a shift in priority when choosing a chemical reaction: the chemical reaction can now be chosen to better elucidate the heavy element chemical properties, rather than concentrating on removal of interfering activities.

In recent experiments, ^{257}Rf, an isotope of element 104 with a 4-second half-life, was produced and separated from other nuclear reaction products by the BGS. After stopping the Rf in a gas cell, it was transported to the chemical separation system with a gas-jet system. Rapid liquid-liquid extractions were carried out with an automated chemistry and detection system. These experiments demonstrated the large increase in sensitivity afforded by the use of the BGS as a preseparator. Taking advantage of these new capabilities, we are presently developing new liquid-liquid extraction and gas-phase chemical systems which will provide new insights into the chemical properties of Rf and Db (element 105).

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[1] Contact: Heino Nitsche, hnitsche @lbl.gov, phone; (510) 486-5615

For future experiments, we will develop a ^{244}Pu target capability for the BGS. Use of this ^{244}Pu target will allow access to longer-lived isotopes of Rf and Db, as well as isotopes of Sg (element 106), Bh (element 107), Hs (element 108), and possibly elements 112 and 114. Chemical reaction systematics of elements 104 through 108, and possibly 112 and 114, will be studied by liquid-liquid solvent extractions with organic extractants having different functional groups and extraction mechanisms; for example, chelate complexation via beta-diketonates and crown ethers, adduct formation with organophosphates, and liquid ion exchange with amines. Additionally, gas phase reactions with highly volatile organic compounds will be performed to measure reaction kinetics and thermodynamic adsorption enthalpies on various surface materials such as quartz and transition metal surfaces.

The combination of the versatile and reliable LBNL 88-Inch Cyclotron, with the world-leading ECR ion source development, and the highly efficient and selective Berkeley Gas-filled Separator, is ideally suited for studies of heavy element chemical properties. The LBNL Heavy Element Nuclear and Radiochemistry program will take full advantage of these new experimental opportunities in the study of the nuclear chemistry of the heaviest elements.

Appendix

Summary of heavy element chemical properties

In the periodic table below, the eight transfermium elements for which chemical studies have been performed are shaded with bright colors. Corresponding lighter colors indicate chemical homologs, which have similar properties. Research by the LBNL Heavy Element Nuclear and Radiochemistry group since 1987 (often in collaboration with European groups) is summarized below.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	25 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 lanthanide series	74 Hf	75 Ta	75 W	77 Re	788 Os	79 Ir	80 Pt	81 Au	82 Hg	83 Tl	84 Pb	85 Bi	86 Po	87 At	88 Rn
87 Fr	88 Ra	89-103 actinide series	104 Rf	105 Db	106 Sg	107 Bh	108 Hs										

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

Previous experiments showed stable Lr^{3+} (element 103) in aqueous solution, demonstrating that Lr is an actinide. In our work we have determined some more detailed chemical properties:

- ✓ Determination of the ionic radius of Lr^{3+} (element 103)
- ✓ Limit on the Lr^{3+} -> Lr^{1+} reduction potential

Early experiments showed stable Rf^{4+} (element 104) in solution and in formation of anionic chloride complexes, showing that Rf is the first transactinide element. Our work has made detailed comparisons with the homologs:

- ✓ Many studies showing formation and extraction of anionic, neutral, and cationic Rf complexes and comparison with Zr^{4+}, Hf^{4+}, Th^{4+}, and Pu^{4+}
- ✓ Gas-phase Rf chlorides and bromides, show the following trend in volatilities: $ZrCl4_{+} \approx RfCl_4 > HfCl_4$. Bromides are less volatile than chlorides with a similar volatility trend: $ZrBr_{4+} \approx RfBr_4 > HfBr_4$.

The only early chemical experiments with Db (element 105) were gas-phase measurements with questionable validity. We have made many measurements in both aqueous and gas phases:

- ✓ First aqueous-phase chemical separations with Db, showing strong adsorption from acidic solutions, establishing the proper position of Db in the periodic table
- ✓ Extraction of Db chloride and fluoride complexes, and comparison with homologs, Nb^{5+}, Ta^{5+}, and Pa^{5+}
- ✓ Gas-phase measurements of Db chlorides and bromides, determining the volatility of $DbCl_5$, $DbOCl_3$, $DbBr_5$, and comparison with $NbCl_5$, $NbOCl_5$, $NbBr_3$, and $TaBr_3$

There were no previous measurements of Sg (element 106) chemical properties. Our first separations included:

- ✓ Gas-phase separations of Sg, showing a trend of decreasing volatility: $MoO_2Cl_2 > WO_2Cl_2 > SgO_2Cl_2$
- ✓ Aqueous-phase cation exchange, showing formation of SgO_4^{2-}, similar to MoO_4^{2-} and WO_4^{2-}, and distinctly different from hexavalent uranium, which forms UO_2^{2+}

We have made the only measurement of Bh (element 107) chemical properties:

- ✓ Gas-phase volatility of group seven oxychlorides decreases according to: $TcO_3Cl > ReO_3Cl > BhO_3Cl$

We have made the only measurement of Hs (element 108) chemical properties:

- ✓ HsO_4 is easily formed, characteristic of group 8. HsO_4 is slightly less volatile than the homolog, OsO_4